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(54) Title: THORIUM-CONTAINING SAPO MOLECULAR SIEVE FOR PRODUCING OLEFINS

(57) Abstract: A silicoaluminophosphate molecular sieve that contains thorium is useful in a method of making a product including an olefin from an oxygenate feedstock. The method includes providing the thorium-containing silicoaluminophosphate catalyst; and contacting the catalyst in its activated state with an oxygenate feedstock under conditions effective to produce an olefin product.

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THORIUM-CONTAINING SAPO MOLECULAR SIEVE FOR PRODUCING OLEFINS

Field of the Invention

5 This invention relates to a silicoaluminophosphate molecular sieve containing thorium and to a method for converting an oxygenate feedstock to a product including an olefin. In particular, this invention is directed to a method for converting an oxygenate feedstock to a product including an olefin by
10 contacting the feedstock with a silicoaluminophosphate molecular sieve containing thorium.

Background of the Invention

 Olefins have traditionally been produced through the process of petroleum cracking. Because of the limited availability and high cost of petroleum sources,
15 the cost of producing olefins from such petroleum sources has the potential to steadily increase. Light olefins such as ethylene and propylene serve as feeds for the production of numerous chemicals and polymers.

 The search for alternative materials for the production of light olefins such as ethylene and propylene has led to the use of oxygenates such as alcohols, and
20 more particularly to methanol and ethanol or their derivatives as feedstocks. These and other alcohols may be produced by fermentation or from synthesis gas. Synthesis gas can be produced from natural gas, petroleum liquids, carbonaceous materials including coal, recycled plastics, municipal wastes, or any organic material. Thus alcohols and alcohol derivatives may provide non-petroleum based
25 routes for hydrocarbon production.

 Silicoaluminophosphates (SAPOs) are structured crystalline molecular sieves which have found application as catalysts. In particular, the use of SAPOs in converting alcohols or ethers to products including olefins, particularly ethylene and propylene, is becoming of greater interest for large scale, commercial
30 production facilities.

 In addition to SAPOs, which are considered non-zeolitic (non-zeolites) molecular sieves, molecular sieves can also be zeolitic (zeolites). Such catalysts

are also used for catalyzing the oxygenate-to-olefin conversion reaction. Zeolitic molecular sieves include, but are not limited to, mordenite, chabazite, erionite, ZSM-5, ZSM-34, ZSM-48 and mixtures thereof. Methods of making these molecular sieves are known in the art. ZSM-5 was the first and most extensively studied catalyst for the conversion of methanol to olefins. Unfortunately, ZSM-5 produces not only the desired light olefins, but also undesired by-products. In particular, ZSM-5 produces aromatics, particularly at high methanol conversion.

In converting oxygenates to light olefin product, by-products are formed. These by-products include alkanes (methane, ethane, propane, and larger), C_4^+ olefins, aromatic compounds, carbon oxides and carbonaceous deposits on and within the catalyst materials (also referred to as "coke").

During conversion of oxygenates to light olefins, carbonaceous deposits accumulate on the catalyst used to promote the conversion reaction. As the amount of these carbonaceous deposits increases, the catalyst begins to lose activity and, consequently, less of the feedstock is converted to the light olefin products. At some point, the build up of these carbonaceous deposits causes the catalyst to reduce its capability to convert the oxygenates to light olefins. Once a catalyst becomes deactivated, it must be removed from the reaction vessel and replaced with activated catalyst. To reduce catalyst costs, activated catalyst is obtained by removing the carbonaceous deposits from the deactivated catalyst. This process is typically referred to as regeneration, and typically takes place in a vessel called a regenerator.

U.S. Patent No. 3,244,766 to Keough teaches a process for ethanol conversion to ethylene with a hydrogen exchanged mordenite catalyst. Keough discloses that such catalyst allows the dehydration of alcohol to occur at temperatures below 300° C.

U.S. Patent No. 4,025,576 to Chang *et al.* teaches a multistage process for converting light alcohols to olefins using certain crystalline zeolites having a high silica:alumina ratio and a constrained access to the crystalline space, for example HSZM-5. Cheng *et al.* indicate that a critical feature of the invention, namely conducting the conversion from alcohol to olefin at subatmospheric partial

pressure of the reactant feed and using certain crystalline zeolites, enhances selectivity for olefin production and permits complete conversion of the alcohol.

U.S. Patent No. 4,752,651 to Kaiser *et al.* discloses a process for converting methanol to olefin (MTO) using non-zeolitic molecular sieves, such as SAPO-34, that contain an element selected from the group consisting of arsenic, beryllium, boron, chromium, cobalt, gallium, germanium, iron, lithium, magnesium, manganese, titanium and zinc.

In the Catalyst Review *Science and Engineering*, vol. 26, no. 3&4, page 323 (1984), C. D. Chang of Mobil Corporation describes a thorium containing ZSM-34. The reaction data describe 100% methanol conversion at a temperature of 400°C and 1 atm pressure and yields of 42.9% ethylene and 33.4% propylene.

In converting oxygenate-containing feedstock to light olefin product, better selectivity to olefin product, such as ethylene and propylene, and especially ethylene selectivity, as well as away from undesirable by-product, is still needed. It is particularly desirable to obtain product high in ethylene and/or propylene content, while reducing the amount of any one or more of the C₁-C₄ paraffin by-products and reducing the amount of coke the reaction deposits on the catalyst.

Summary of the Invention

In order to overcome various problems presently inherent in the art, this invention provides various embodiments of a molecular sieve and catalyst and of a method for continuous production of product including an olefin from an oxygenate-containing feedstock. In one embodiment, the catalyst is a crystalline silicoaluminophosphate molecular sieve comprising a silicoaluminophosphate framework and thorium. Preferably, the atomic ratio of silicon in the silicoaluminophosphate framework to thorium is from about 0.01:1 to about 1000:1, more preferably from about 0.1:1 to about 500:1, and most preferably from about 0.5:1 to about 50:1.

In a particular embodiment, the invention is directed to a catalyst for converting an oxygenate feedstock to a product including an olefin, comprising the crystalline silicoaluminophosphate molecular sieve and a binder.

The thorium-containing SAPO catalyst is of great benefit in large scale commercial processes of making olefin product from oxygenate feedstock, particularly making olefins containing ethylene or propylene from feedstock comprising methanol or dimethyl ether. The method of making a product including an olefin from an oxygenate feedstock, comprises contacting a silicoaluminophosphate molecular sieve having a silicoaluminophosphate framework and thorium with an oxygenate feedstock under conditions effective to convert the feedstock to the product including an olefin. In another embodiment, the invention provides a product including an olefin made according to this method.

In yet another embodiment, the invention provides a method of making a polyolefin from an oxygenate feedstock, comprising contacting a silicoaluminophosphate molecular sieve described above with an oxygenate feedstock under conditions effective to convert the feedstock to an olefin product, and contacting the olefin product with a polyolefin-forming catalyst under conditions effective to form the polyolefin. Another embodiment of the invention is directed to a polyolefin made by this process. Preferably, the polyolefin comprises polyethylene or polypropylene.

In the embodiments, the silicoaluminophosphate molecular sieve is preferably selected from the group consisting of SAPO-5, SAPO-8, SAPO-11, SAPO-16, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-36, SAPO-37, SAPO-40, SAPO-41, SAPO-42, SAPO-44, SAPO-47, SAPO-56, the metal containing forms thereof and mixtures thereof. More particularly, the silicoaluminophosphate is selected from the group including SAPO-5, SAPO-11, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34 and SAPO-44. Most particularly, the preferred silicoaluminophosphate is SAPO-34.

The oxygenate feedstock is preferably selected from the group consisting of methanol; ethanol; n-propanol; isopropanol; C₄-C₂₀ alcohols; methyl ethyl ether; dimethyl ether; diethyl ether; di-isopropyl ether; formaldehyde; dimethyl carbonate; dimethyl ketone; acetic acid; and mixtures thereof. More preferably, the oxygenate feedstock is methanol, dimethyl ether, or a mixture thereof.

In order to convert the oxygenate to olefin product, the process is preferably performed at a temperature between 200°C and 600°C.

Detailed Description of the Invention

5 The silicoaluminophosphate molecular sieves of this invention comprise a three-dimensional microporous crystal framework structure of $[\text{SiO}_2]$, $[\text{AlO}_2]$ and $[\text{PO}_2]$ corner sharing tetrahedral units. The way Si is incorporated into the structure can be determined by ^{29}Si MAS NMR. See Blackwell and Patton, *J. Phys. Chem.*, 92, 3965 (1988). The desired SAPO molecular sieves will exhibit
10 one or more peaks in the ^{29}Si MAS NMR, with a chemical shift $\delta(\text{Si})$ in the range of -88 to -94 ppm and with a combined peak area in that range of at least 20% of the total peak area of all peaks with a chemical shift $\delta(\text{Si})$ in the range of -88 ppm to -115 ppm, where the $\delta(\text{Si})$ chemical shifts refer to external tetramethylsilane (TMS).

15 Silicoaluminophosphate molecular sieves are generally classified as being microporous materials having 8, 10, or 12 membered ring structures. These ring structures can have an average pore size ranging from about 3.5-15 angstroms. Preferred are the small pore SAPO molecular sieves having an average pore size ranging from about 3.5 to 5 angstroms, more preferably from 4.0 to 5.0 angstroms.
20 These preferred pore sizes are typical of molecular sieves having 8 membered rings.

 In general, silicoaluminophosphate molecular sieves comprise a molecular framework of corner-sharing $[\text{SiO}_2]$, $[\text{AlO}_2]$, and $[\text{PO}_2]$ tetrahedral units. This type of framework is effective in converting various oxygenates into olefin
25 products.

 The $[\text{PO}_2]$ tetrahedral units within the framework structure of the molecular sieve of this invention can be provided by a variety of compositions. Examples of these phosphorus-containing compositions include phosphoric acid, organic phosphates such as triethyl phosphate, and aluminophosphates. The
30 phosphorous-containing compositions are mixed with reactive silicon and aluminum-containing compositions under the appropriate conditions to form the molecular sieve.

The $[\text{AlO}_2]$ tetrahedral units within the framework structure can be provided by a variety of compositions. Examples of these aluminum-containing compositions include aluminum alkoxides such as aluminum isopropoxide, aluminum phosphates, aluminum hydroxide, sodium aluminate, and pseudoboehmite. The aluminum-containing compositions are mixed with reactive silicon and phosphorus-containing compositions under the appropriate conditions to form the molecular sieve.

The $[\text{SiO}_2]$ tetrahedral units within the framework structure can be provided by a variety of compositions. Examples of these silicon-containing compositions include silica sols and silicium alkoxides such as tetra ethyl orthosilicate. The silicon-containing compositions are mixed with reactive aluminum and phosphorus-containing compositions under the appropriate conditions to form the molecular sieve.

Suitable silicoaluminophosphate molecular sieves include SAPO-5, SAPO-8, SAPO-11, SAPO-16, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-36, SAPO-37, SAPO-40, SAPO-41, SAPO-42, SAPO-44, SAPO-47, SAPO-56, the metal containing forms thereof, and mixtures thereof. Preferred are SAPO-5, SAPO-8, SAPO-11, SAPO-16, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-36, SAPO-37, SAPO-40, SAPO-41, SAPO-42, SAPO-44, SAPO-47, SAPO-56 and mixtures thereof. More particularly, the silicoaluminophosphate is selected from the group including SAPO-5, SAPO-11, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34, SAPO-44 and mixtures thereof. Most particularly, the preferred silicoaluminophosphate is selected from the group consisting of SAPO-18, SAPO-34 and mixtures thereof. As used herein, the term mixture is synonymous with combination and is considered a composition of matter having two or more components in varying proportions, regardless of their physical state.

The silicoaluminophosphate molecular sieves are synthesized by hydrothermal crystallization methods generally known in the art. See, for example, U.S. Pat. Nos. 4,440,871; 4,861,743; 5,096,684; and 5,126,308, the methods of making of which are fully incorporated herein by reference. A reaction mixture is formed by mixing together reactive silicon, aluminum and

phosphorus components, along with at least one template. Generally the mixture is sealed and heated, preferably under autogenous pressure, to a temperature of at least 100°C, preferably from 100-250°C, until a crystalline product is formed.

Formation of the crystalline product can take anywhere from around 2 hours to as much as 2 weeks. In some cases, stirring or seeding with crystalline material will facilitate the formation of the product.

Typically, the molecular sieve product will be formed in solution. It can be recovered by standard means, however, such as by centrifugation or filtration. The product can also be washed, recovered by the same means and dried.

As a result of the crystallization process, the recovered sieve contains within its pores at least a portion of the template used in making the initial reaction mixture. The crystalline structure essentially wraps around the template, and the template must be removed to obtain catalytic activity. Once the template is removed, the crystalline structure that remains has what is typically called an intracrystalline pore system.

The SAPO molecular sieve can contain one or more templates. Templates are structure directing or affecting agents, and typically contain nitrogen, phosphorus, oxygen, carbon, hydrogen or a combination thereof, and can also contain at least one alkyl or aryl group, with 1 to 8 carbons being present in the alkyl or aryl group. Mixtures of two or more templates can produce mixtures of different sieves or predominantly one sieve where one template is more strongly directing than another.

Representative templates include tetraethyl ammonium salts, cyclopentylamine, aminomethyl cyclohexane, piperidine, triethylamine, cyclohexylamine, tri-ethyl hydroxyethylamine, morpholine, dipropylamine (DPA), pyridine, isopropylamine and combinations thereof. Preferred templates are triethylamine, cyclohexylamine, piperidine, pyridine, isopropylamine, tetraethyl ammonium salts, and mixtures thereof. The tetraethylammonium salts include tetraethyl ammonium hydroxide (TEAOH), tetraethyl ammonium phosphate, tetraethyl ammonium fluoride, tetraethyl ammonium bromide, tetraethyl ammonium chloride, tetraethyl ammonium acetate. Preferred tetraethyl

ammonium salts are tetraethyl ammonium hydroxide and tetraethyl ammonium phosphate.

As is known in the art, molecular sieve or catalyst containing the molecular sieve, must be activated prior to use in a catalytic process. Activation is performed in such a manner that template is removed from the molecular sieve, leaving active catalytic sites with the microporous channels of the molecular sieve open for contact with feed. The activation process is typically accomplished by calcining, or essentially heating the template at a temperature of from 200 to 800°C in the presence of an oxygen-containing gas. In some cases, it may be desirable to heat in an environment having a low oxygen concentration. This type of process can be used for partial or complete removal of the template from the intracrystalline pore system. In other cases, particularly with smaller templates, complete or partial removal from the sieve can be accomplished by conventional desorption processes such as those used in making standard zeolites.

The silicoaluminophosphate molecular sieves may be admixed (blended) with other materials. When blended, the resulting composition is typically referred to as a silicoaluminophosphate (SAPO) catalyst, with the catalyst comprising the SAPO molecular sieve.

Materials which can be blended with the molecular sieve can be various inert or catalytically active materials, or various binder materials. These materials include compositions such as kaolin and other clays, various forms of rare earth metals, other non-zeolite catalyst components, zeolite catalyst components, alumina or alumina sol, titania, zirconia, quartz, silica or silica sol, and mixtures thereof. These components are also effective in reducing overall catalyst cost, acting as a thermal sink to assist in heat shielding the catalyst during regeneration, densifying the catalyst and increasing catalyst strength. When blended with non-silicoaluminophosphate molecular sieve materials, the amount of molecular sieve which is contained in the final catalyst product ranges from 10 to 90 weight percent of the total catalyst, preferably 30 to 70 weight percent of the total catalyst.

Additional olefin-forming molecular sieve materials can be mixed with the silicoaluminophosphate catalyst if desired. Several types of molecular sieves

exist, each of which exhibit different properties. Structural types of small pore molecular sieves that are suitable for use in this invention include AEL, AFT, APC, ATN, ATT, ATV, AWW, BIK, CAS, CHA, DDR, EDI, ERI, GOO, KFI, LEV, LTA, MON, PAU, PHI, RHO, THO, and substituted forms thereof.

5 Structural types of medium pore molecular sieves that are suitable for use in this invention include MFI, MEL, MTW, EUO, MTT, HEU, FER, AFO, AEL, TON, and substituted forms thereof. These small and medium pore molecular sieves are described in greater detail in the *Atlas of Zeolite Structural Types*, W.M. Meier and D.H. Olsen, Butterworth Heineman, 3rd ed., 1997, the detailed description of
10 which is explicitly incorporated herein by reference. Preferred molecular sieves which can be combined with a silicoaluminophosphate catalyst include ZSM-5, ZSM-34, erionite, and chabazite.

Thorium can be incorporated into the SAPO catalyst through any one of the standard methods well known to those skilled in the art. For example,
15 thorium can be incorporated by ion-exchange, impregnation, or direct synthesis methods.

In one embodiment, thorium is incorporated by ion exchange. In an ion exchange process, a solution of thorium is first made by dissolving the desired amount of a thorium-containing compound in water under mild conditions.
20 Preferably, the water is de-ionized. The temperature of mixing is dependent upon the thorium-containing compound's solubility in water, or whatever other medium is selected. The process may be conducted under pressure or at atmospheric pressure. After adequate mixing, the solution is then added to the selected amount of the molecular sieve. The resulting mixture is stirred as required. In some
25 cases, stirring is not required and the mixture may be left undisturbed for a time adequate to permit the desired level of incorporation. The catalyst product is then filtered, optionally washed, dried, and calcined by methods well known to those skilled in the art.

In another embodiment, thorium is impregnated into the SAPO molecular sieve. In an impregnation process, a limited amount of water solution of the
30 thorium-containing compound is dripped into the molecular sieve such that all the solution is totally absorbed and there is no excess solution, i.e., all the thorium in

the solution ends up in the molecular sieve. The molecular sieve is vigorously tumbled while adding the loading solution to uniformly distribute the metal.

Alternatively, thorium containing catalysts can be synthesized by hydrothermal crystallization for an effective time at an effective pressure and temperatures from a reaction mixture containing active resources of thorium, silicon, aluminum and phosphorous, and preferably organic templating. The reaction mixture is generally placed in a sealed pressure vessel, preferable lined with an inert plastic material such as polytetrafluoroethylene (PTFE) and heated, preferably under autogenous pressure at a temperature between 50 °C and 250 °C, and preferably between 100-200 °C, until crystals of the ThSAPO product are obtained, usually about a period of from hours to several weeks. Generally the crystallization time is from about 2 hours to about 30 days and typically from about 4 hours to about 20 days. The product is then recovered by any suitable method such as centrifugation or filtration.

The amount of thorium which is incorporated into the molecular sieve may vary over a wide range depending, at least in part, on the selected molecular sieve catalyst and the incorporation method. The amount of thorium incorporated is measured on an atomic thorium basis in terms of silicon to thorium ratio. The silicon to thorium atomic ratios are in the range from about 0.01:1 to about 1000:1, preferably from about 0.1:1 to about 500:1, and most preferably from about 0.5:1 to about 50:1.

In converting oxygenate-containing feedstock to product including light olefins, an ongoing need exists to further enhance the selectivity to ethylene and/or propylene, especially ethylene, to reduce C₁-C₄ paraffin by-products, and to reduce the amount of coke deposits formed on the catalyst during reaction.

The addition of thorium to a SAPO molecular sieve enhances the selectivity of ethylene and propylene, especially ethylene produced from the conversion of oxygenate-containing feedstock such as methanol, to olefins. Further, the presence of thorium reduces the amount of undesirable by-products such as C₁-C₄ paraffin and reduces the amount of coke the reaction deposits on the catalyst.

In one embodiment of this invention, a feed containing an oxygenate is contacted in a reaction zone of a reactor apparatus with an activated molecular sieve catalyst at process conditions effective to produce light olefins, i.e., an effective temperature, pressure, WHSV (weight hour space velocity) and, optionally, an effective amount of diluent, correlated to produce light olefins. Typically, the oxygenate feed is contacted with the catalyst when the oxygenate is in a vapor phase. However, the process may be carried out in a liquid or a mixed vapor/liquid phase. When the process is carried out in a liquid phase or a mixed vapor/liquid phase, different conversions and selectivities of feed-to-product may result depending upon the catalyst and reaction conditions.

Olefins can generally be produced at a wide range of temperatures. An effective operating temperature range can be from about 200°C to 700°C. At the lower end of the temperature range, the formation of the desired olefin products may become markedly slow. At the upper end of the temperature range, the process may not form an optimum amount of product. An operating temperature of at least 300°C, and up to 600°C is preferred.

Owing to the nature of the process, it may be desirable to carry out the process of the present invention by use of the molecular sieve catalysts in a dynamic bed system or any system of a variety of transport beds rather than in a fixed bed system. It is particularly desirable to operate the reaction process at high space velocities.

The conversion of oxygenates to produce light olefins may be carried out in a variety of large scale catalytic reactors, including, but not limited to, fluid bed reactors and concurrent riser reactors as described in "Free Fall Reactor," *Fluidization Engineering*, D. Kunii and O. Levenspiel, Robert E. Krieger Publishing Co. NY, 1977, incorporated in its entirety herein by reference. Additionally, countercurrent free fall reactors may be used in the conversion process. See, for example, US-A-4,068,136 and "Riser Reactor", *Fluidization and Fluid-Particle Systems*, pages 48-59, F.A. Zenz and D. F. Othmo, Reinhold Publishing Corp., NY 1960, the descriptions of which are expressly incorporated herein by reference.

Any standard commercial scale reactor system can be used, including fixed bed or moving bed systems. The commercial scale reactor systems can be operated at a weight hourly space velocity (WHSV) of from 1 hr⁻¹ to 1000 hr⁻¹. In the case of commercial scale reactors, WHSV is defined as the weight of hydrocarbon in the feed per hour per weight of silicoaluminophosphate molecular sieve content of the catalyst. The hydrocarbon content will be oxygenate and any hydrocarbon which may optionally be combined with the oxygenate. The silicoaluminophosphate molecular sieve content is intended to mean only the silicoaluminophosphate molecular sieve portion that is contained within the catalyst. This excludes components such as binders, diluents, inerts, rare earth components, etc.

It is highly desirable to operate at a temperature of at least 300°C and a Temperature Corrected Normalized Methane Sensitivity (TCNMS) of less than about 0.016, preferably less than about 0.012, more preferably less than about 0.01. It is particularly preferred that the reaction conditions for making olefin from oxygenate comprise a WHSV of at least about 20 hr⁻¹ producing olefins and a TCNMS of less than about 0.016.

As used herein, TCNMS is defined as the Normalized Methane Selectivity (NMS) when the temperature is less than 400°C. The NMS is defined as the methane product yield divided by the ethylene product yield wherein each yield is measured on, or is converted to, a weight % basis. When the temperature is 400°C or greater, the TCNMS is defined by the following equation, in which T is the average temperature within the reactor in °C:

$$\text{TCNMS} = \frac{\text{NMS}}{1 + (((T-400)/400) \times 14.84)}$$

The pressure also may vary over a wide range, including autogenous pressures. Effective pressures may be in, but are not necessarily limited to, pressures of from about 0.1 kPa to about 10 MPa. Preferred pressures are in the range of about 5 kPa to about 5 MPa, with the most preferred range being of from about 50 kPa to about 0.5 MPa. The foregoing pressures are exclusive of any

oxygen depleted diluent, and thus, refer to the partial pressure of the oxygenate compounds and/or mixtures thereof with feedstock. At the lower and upper end of the foregoing pressure ranges, the rate of selectivity, conversion and/or reaction may not be optimum.

5 One or more inert diluents may be present in the feedstock, for example, in an amount of from 1 to 99 molar percent, based on the total number of moles of all feed and diluent components fed to the reaction zone (or catalyst). As defined herein, diluents are compositions which are essentially non-reactive across a molecular sieve catalyst, and primarily function to make the oxygenates in the
10 feedstock less concentrated. Typical diluents include, but are not necessarily limited to helium, argon, nitrogen, carbon monoxide, carbon dioxide, hydrogen, water, paraffins, alkanes (especially methane, ethane, and propane), alkylenes, aromatic compounds, and mixtures thereof. The preferred diluents are water and nitrogen. Water can be injected in either liquid or vapor form.

15 The process may be carried out in a batch, semi-continuous or continuous fashion. The process can be conducted in a single reaction zone or a number of reaction zones arranged in series or in parallel.

 The level of conversion of the oxygenates can be maintained to reduce the level of unwanted by-products. Conversion can also be maintained sufficiently
20 high to avoid the need for commercially undesirable levels of recycling of unreacted feeds. A reduction in unwanted by-products is seen when conversion moves from 100 mol % to about 98 mol % or less. Recycling up to as much as about 50 mol % of the feed is commercially acceptable. Therefore, conversions levels which achieve both goals are from about 50 mol % to about 98 mol % and,
25 desirably, from about 85 mol % to about 98 mol %. However, it is also acceptable to achieve conversion between 98 mol % and 100 mol % in order to simplify the recycling process. Oxygenate conversion may be maintained at this level using a number of methods familiar to persons of ordinary skill in the art. Examples include, but are not necessarily limited to, adjusting one or more of the following:
30 the reaction temperature; pressure; flow rate (i.e., WHSV); level and degree of catalyst regeneration; amount of catalyst re-circulation; the specific reactor

configuration; the feed composition; and other parameters which affect the conversion.

If regeneration is required, the molecular sieve catalyst can be continuously introduced as a moving bed to a regeneration zone where it can be regenerated, such as for example by removing carbonaceous materials or by oxidation in an oxygen-containing atmosphere. In a preferred embodiment, the catalyst is subject to a regeneration step by burning off carbonaceous deposits accumulated during the conversion reactions.

The oxygenate feedstock comprises at least one organic compound which contains at least one oxygen atom, such as aliphatic alcohols, ethers, carbonyl compounds (aldehydes, ketones, carboxylic acids, carbonates, esters and the like). When the oxygenate is an alcohol, the alcohol can include an aliphatic moiety having from 1 to 10 carbon atoms, more preferably from 1 to 4 carbon atoms. Representative alcohols include but are not necessarily limited to lower straight and branched chain aliphatic alcohols, their unsaturated counterparts and the nitrogen, halogen and sulfur analogues of such. Examples of suitable oxygenate compounds include, but are not limited to: methanol; ethanol; n-propanol; isopropanol; C₄ - C₂₀ alcohols; methyl ethyl ether; dimethyl ether; diethyl ether; di-isopropyl ether; formaldehyde; dimethyl carbonate; dimethyl ketone; acetic acid; and mixtures thereof. Preferred oxygenate compounds are methanol, dimethyl ether, or a mixture thereof.

The method of making the preferred olefin product in this invention can include the additional step of making these compositions from hydrocarbons such as oil, coal, tar sand, shale, biomass and natural gas. Methods for making the compositions are known in the art. These methods include fermentation to alcohol or ether, making synthesis gas, then converting the synthesis gas to alcohol or ether. Synthesis gas can be produced by known processes such as steam reforming, autothermal reforming and partial oxidization.

Ethylene and propylene are selectively produced from an oxygenate using the catalyst according to the invention. Such selectivity of ethylene plus propylene is from 50%-95% of the feeds' hydrocarbon content. Preferably the selectivity of ethylene and propylene is 70-95%, and more preferably 80-95%.

One skilled in the art will also appreciate that the olefins produced by the oxygenate-to-olefin conversion reaction of the present invention can be polymerized to form polyolefins, particularly polyethylene and polypropylene. Processes for forming polyolefins from olefins are known in the art. Catalytic processes are preferred. Particularly preferred are metallocene, Ziegler/Natta and acid catalytic systems. See, for example, U.S. Patent Nos. 3,258,455; 3,305,538; 3,364,190; 5,892,079; 4,659,685; 4,076,698; 3,645,992; 4,302,565; and 4,243,691, the catalyst and process descriptions of each being expressly incorporated herein by reference. In general, these methods involve contacting the olefin product with a polyolefin-forming catalyst at a pressure and temperature effective to form the polyolefin product.

A preferred polyolefin-forming catalyst is a metallocene catalyst. The preferred temperature range of operation is between 50 and 240°C and the reaction can be carried out at low, medium or high pressure, being anywhere within the range of about 1 to 200 bars. For processes carried out in solution, an inert diluent can be used, and the preferred operating pressure range is between 10 and 150 bars, with a preferred temperature range of between 120 and 230°C. For gas phase processes, it is preferred that the temperature generally be within a range of 60 to 160°C, and that the operating pressure be between 5 and 50 bars.

In addition to polyolefins, numerous other olefin derivatives may be formed from the olefins recovered therefrom. These include, but are not limited to, aldehydes, alcohols, acetic acid, linear alpha olefins, vinyl acetate, ethylene dichloride and vinyl chloride, ethylbenzene, ethylene oxide, cumene, isopropyl alcohol, acrolein, allyl chloride, propylene oxide, acrylic acid, ethylene-propylene rubbers, and acrylonitrile, and trimers and dimers of ethylene, propylene or butylenes. The methods of manufacturing these derivatives are well known in the art, and therefore, are not discussed herein.

Having now fully described this invention, it will be appreciated by those skilled in the art that the invention can be performed within a wide range of parameters within what is claimed, without departing from the spirit and scope of the invention.

What is claimed is:

- 1 1. A crystalline silicoaluminophosphate molecular sieve comprising a
2 silicoaluminophosphate framework and thorium.
- 1 2. The crystalline silicoaluminophosphate molecular sieve of claim 1,
2 wherein an atomic ratio of silicon in the silicoaluminophosphate framework to
3 thorium is from about 0.01:1 to about 1000:1.
- 1 3. The crystalline silicoaluminophosphate molecular sieve of claim 2,
2 wherein the ratio is from about 0.1:1 to about 500:1.
- 1 4. The crystalline silicoaluminophosphate molecular sieve of claim 3,
2 wherein the ratio is from about 0.5:1 to about 50:1.
- 1 5. The crystalline silicoaluminophosphate molecular sieve of claim 1,
2 wherein the silicoaluminophosphate framework is selected from the group
3 consisting of SAPO-5, SAPO-8, SAPO-11, SAPO-16, SAPO-17, SAPO-18,
4 SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-36, SAPO-37, SAPO-40,
5 SAPO-41, SAPO-42, SAPO-44, SAPO-47, SAPO-56, the metal containing forms
6 thereof, and mixtures thereof.
- 1 6. The crystalline silicoaluminophosphate molecular sieve of claim 5
2 wherein the silicoaluminophosphate framework is selected from the group
3 consisting of SAPO-5, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34,
4 SAPO-44, and mixtures thereof.
- 1 7. The crystalline silicoaluminophosphate molecular sieve of claim 6,
2 wherein the silicoaluminophosphate framework is selected from the group
3 consisting of SAPO-18, SAPO-34 and mixtures thereof.
- 1 8. A catalyst for converting an oxygenate feedstock to a product
2 including an olefin, comprising a crystalline silicoaluminophosphate molecular
3 sieve, having a silicoaluminophosphate framework and thorium, and a binder.

1 9. The catalyst defined in claim 8, wherein an atomic ratio of silicon
2 in the silicoaluminophosphate framework to thorium is from about 0.01:1 to about
3 1000:1.

1 10. The catalyst of claim 9, wherein the ratio is from about 0.1:1 to
2 about 500:1.

1 11. The catalyst of claim 10, wherein the ratio is from about 0.5:1 to
2 about 50:1.

1 12. The catalyst of claim 8, wherein the silicoaluminophosphate
2 molecular sieve is selected from the group consisting of SAPO-5, SAPO-8,
3 SAPO-11, SAPO-16, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34,
4 SAPO-35, SAPO-36, SAPO-37, SAPO-40, SAPO-41, SAPO-42, SAPO-44,
5 SAPO-47, SAPO-56, the metal containing forms thereof, and mixtures thereof.

1 13. The catalyst of claim 12, wherein the silicoaluminophosphate
2 framework is selected from the group consisting of SAPO-5, SAPO-17, SAPO-18,
3 SAPO-20, SAPO-31, SAPO-34 and SAPO-44.

1 14. The catalyst of claim 13, wherein the silicoaluminophosphate
2 framework is SAPO-34.

1 15. A method of making a product including an olefin from an
2 oxygenate feedstock, comprising:
3 contacting a silicoaluminophosphate molecular sieve having a
4 silicoaluminophosphate framework and thorium with an oxygenate feedstock
5 under conditions effective to convert the feedstock to the product including the
6 olefin.

1 16. The method of claim 15, wherein an atomic ratio of silicon in the
2 silicoaluminophosphate framework to thorium is from about 0.01:1 to about
3 1000:1.

1 17. The method of claim 16, wherein the ratio is from about 0.1:1 to
2 about 500:1.

1 18. The method of claim 17, wherein the ratio is from about 0.5:1 to
2 about 50:1.

1 19. The method of claim 15, wherein the silicoaluminophosphate
2 molecular sieve is selected from the group consisting of SAPO-5, SAPO-8,
3 SAPO-11, SAPO-16, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34,
4 SAPO-35, SAPO-36, SAPO-37, SAPO-40, SAPO-41, SAPO-42, SAPO-44,
5 SAPO-47, SAPO-56, the metal containing forms thereof, and mixtures thereof.

1 20. The method of claim 19, wherein the silicoaluminophosphate
2 framework is selected from the group consisting of SAPO-5, SAPO-17, SAPO-18,
3 SAPO-20, SAPO-31, SAPO-34, SAPO-44, and mixtures thereof.

1 21. The catalyst of claim 20, wherein the silicoaluminophosphate
2 framework is selected from the group consisting of SAPO-18, SAPO-34 and
3 mixtures thereof.

1 22. An olefin product made according to the method of claim 15.

1 23. The olefin product of claim 22 comprising ethylene and propylene.

1 24. A method of making a polyolefin from an oxygenate feedstock,
2 comprising:

3 contacting a silicoaluminophosphate molecular sieve having a
4 silicoaluminophosphate framework and thorium with an oxygenate feedstock
5 under conditions effective to convert the feedstock to an olefin product, and
6 contacting the olefin product with a polyolefin-forming catalyst under
7 conditions effective to form the polyolefin.

1 25. A polyolefin made by the process of claim 24.

1 26. The polyolefin of claim 25 comprising polyethylene.

- 1 27. The polyolefin of claim 25 comprising polypropylene.

INTERNATIONAL SEARCH REPORT

In **national** Application No
PCT/US 01/04667

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J29/85 C07C1/20 C07C11/02 C10G3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C07C C10G C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 29370 A (EXXON CHEMICAL PATENTS INC) 9 July 1998 (1998-07-09) claims 1-3, 5-13 page 2, line 15 - page 7, line 30	1-27
X	WO 86 00297 A (UNION CARBIDE CORP) 16 January 1986 (1986-01-16) example 3	1-6, 8-13

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/04667

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9829370 A	09-07-1998	AU 5725898 A	31-07-1998
		EP 0960089 A	01-12-1999
		NO 993162 A	25-06-1999
		ZA 9711646 A	07-12-1998
WO 8600297 A	16-01-1986	US 4556645 A	03-12-1985
		AT 35976 T	15-08-1988
		AU 590208 B	02-11-1989
		AU 4549585 A	24-01-1986
		BR 8506801 A	25-11-1986
		CA 1258669 A	22-08-1989
		DE 3563956 D	01-09-1988
		EP 0188530 A	30-07-1986
		JP 61502897 T	11-12-1986
		US 4617320 A	14-10-1986
		ZA 8504826 A	26-02-1986